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#### (54) ROLLER CONSTRUCTION

- (71) We, CESKOSLOVENSKA AKADEMIE VED, a Czechoslovak Corporation, of No. 3 Národní, Praha 1, Czechoslovakia, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The invention relates to a roller with an elastic surface layer particularly suitable for dye application or printing on glass or other materials, such as paper, or plastics, and to a method for its manufacture. The roller consists of a cylindrical core made of a material which does not swell in water, such as metal, plastics material, hard rubber or ceramics, and an outer cylindrical jacket made of a gel comprising a copolymer of acrylonitrile and at least one further monomer selected from simple and substituted acrylamide or methacrylamide, acrylic and methacrylic acid, ethylenesulfonic acid or salts of the above acids, and a swelling agent, which contains at least one compound selected from water, alkylene glycols and polyalkylene glycols, where alkylene is ethylene, propylene or butylene, their methoxy and ethoxy derivatives, glycerol and its acetyl derivatives, phenols, aromatic alcohols, hydro-aromatic alcohols, aliphatic alcohols  $C_1-C_{14}$  and esters of the above alcohols and ethers, fatty acids and their salts and esters, and is desired with a minor amount of dimethylformamide, dimethylsulfoxide or cyclic ethylene carbonate. The invention relates also to a method of manufacturing said roller.
- A method is known for the application of dyes (e.g. dispersions of rare metals) onto the edges of glasses, or tumblers by means of rollers covered with swollen gelatine. Rollers covered with a low-crosslinked polymer of 2-hydroxyethyl methacrylate are much more useful and last substantially longer than the gelatine rollers. The hydrogel layer has to be sufficiently thick to damp impacts in a rapid automated production, otherwise the glasses could often get broken and the production would be interrupted. In addition to this, the hydrogel layer has to be compatible with the dyes used, e.g. gold or platinum dispersions in ethereal oils, and must be well wetted by these dispersions. The hydrogel properties should not change during use, e.g. by drying. Therefore, higher boiling plasticizers, as ethylene glycol or glycerol, are used to swell the gel instead of water. The relatively high cost is disadvantageous for rollers covered with crosslinked 2-hydroxyethyl methacrylate polymer. This is due to the process where the monomer mixture is allowed to polymerize directly on a roller provided with a textile layer, and where the hydrogel layer formed is then machined in a frozen state to be entirely homogeneous and smooth on its surface. For this purpose, the layer is maintained in a cooling mixture of an inert solvent, e.g. toluene with solid carbon dioxide, in intervals between short periods of machining. Carbon dioxide strips a lot of toluene into the atmosphere and the work is unhealthy and connected with fire hazard. Solvents other than hydrocarbons cannot be used, either because of swelling of the polymer which prevents machining, or because of their even higher volatility and harmfulness in comparison with toluene.
- These disadvantages are overcome by the present invention which provides a roller comprising a cylindrical core formed of a material which does not swell in the water, and an outer cylindrical jacket made from a water-insoluble elastic gel comprising a copolymer of acrylonitrile and at least one further monomer selected from simple or substituted acrylamide and methacrylamide, acrylic and methacrylic acid, ethylenesulfonic

[Price 33p]



acid or salts of the aforesaid acids, and a swelling agent which contains at least one compound selected from water, alkylene glycols and polyalkylene glycols, where  
5 alkylene is ethylene, propylene or butylene, their methoxy and ethoxy derivatives, glycerol and its acetyl derivatives, phenols, aromatic alcohols, hydroaromatic alcohols, aliphatic alcohols  $C_1-C_{14}$  and esters of the  
10 aforesaid alcohols and esters, fatty acids and their salts and esters.

Preferably the cylindrical core is formed by metal, plastics material, hard rubber or ceramic material, and the swelling agent may  
15 contain a minor amount of dimethyl formamide, dimethyl sulphoxide or cyclic ethylene carbonate.

The invention further relates to a method of manufacture of this roller, wherein a  
20 layer of the copolymer in a solvent is applied onto the cylindrical core and the copolymer is coagulated in a bath which contains a coagulant comprising at least one compound selected from water, lower aliphatic alcohols  
25  $C_1-C_4$ , acetone, dioxane, benzylalcohol, alkylene glycols  $C_2-C_4$  and polyalkylene glycols, alkylene glycol methoxy and ethoxy derivatives, glycerol and its acetyl derivatives, wherein the copolymer solvent or the  
30 coagulant constitutes said swelling agent, or the roller is subsequently treated with said swelling agent. The copolymer solution may be applied layer by layer, while each layer is applied after the preceding layer has been  
35 coagulated and the excess of the coagulating solution has been removed.

Advantageously, the core is rotated about its axis which is horizontally orientated, the copolymer solution is applied to the rotating  
40 roller at one region and the layer formed is brought into contact with the coagulating liquid at another region. After the coagulation has been completed, or during coagulation, the copolymer is, if desired, cross-  
45 linked by an agent selected from cations of trivalent chromium, trivalent aluminium, trivalent iron, univalent copper, univalent silver, aldehydes and polyisocyanates. Either all the surface or only certain parts thereof  
50 are treated with the above cross-linking agents.

After coagulation, the roller surface or a part thereof may be also treated with other (non cross-linking) agents, as mineral acids,  
55 aqueous hydroxide solution, nitrous acid, or thionyl chloride and then hydroxylamine, to change the properties of the surface, particularly its wettability and swellability.

Each layer applied to the core of the roller is coagulated in a suitable bath which  
60 removes the solvent but does not dissolve the polymer, and the excess coagulation liquid is removed before application of a further layer. If thinner layers are chosen,  
65 the roller can revolve more rapidly. The

thin layers are more suitable, namely because their complete coagulation takes place along a short path in the bath and also the excess coagulating liquid is more easily removed  
70 after coagulation and prior to the application of a further layer of the polymer solution, e.g. by blowing, with a gas, or by contact with a porous elastic cylinder, or filtration paper. The thickness of the last applied layer  
75 is preferably further reduced, so that the end of the application is not perceptible on the surface and a final machining can be avoided.

The hydrogel layer obtained in this way is about 5 to 20 times stronger than the previously used layers of polymeric slightly  
80 cross-linked 2-hydroxyethyl methacrylate and its manufacture is much easier and not connected with toxicity or fire and explosion hazard. The layer is highly elastic and lasts substantially longer in operation. The co-  
85 polymer can be obtained by the partial hydrolysis of polyacrylonitrile to give an acrylonitrile/acrylamide copolymer, and the softness of the layer can be readily adjusted both by the degree of hydrolysis of poly-  
90 acrylonitrile and by the composition of the swelling agent. The swelling agent, which maintains the elastic and swollen state of the gel, is advantageously anhydrous or almost  
95 anhydrous and does not contain another more volatile swelling agent, to preserve the elasticity and softness and protect the layer from drying even after several hours of operation. Ethylene glycol, diacetone, glycerol and similar swelling agents are prefer-  
100 ably applied initially in presence of some water, to prevent temporary dehydration and hardening; only then is the content of water gradually reduced by applying less diluted  
105 solvent of polyacrylonitrile, such as dimethylsulfoxide, dimethylformamide or cyclic ethylene carbonate may be added in minor amounts.

The swelling agent must not be trans-  
110 formed into a solvent by addition of too large amounts of the above solvents. Most of the solvents and precipitants for polyacrylonitrile having a high boiling temperature, such as glycerol, ethylene glycol, di-  
115 ethylene glycol, or dimethylsulfoxide, are hygroscopic and absorb as much water from the atmosphere to achieve an equilibrium state between the solvent and atmosphere. Because the atmospheric humidity changes  
120 unceasingly, it is convenient to add water at the beginning in such amount which corresponds about to the average relative humidity of air. An approximately stable content of  
125 water is attained in this way if the air humidity oscillates around the normal value. Water *per se*, in combination with the aforesaid mixtures of high-boiling liquids, acts favourably upon the quality of the swollen  
130 polymer and it is recommended therefore to

keep at least average and, if possible, constant air humidity in the operation room.

Gilding paints, consisting of dispersions of gold in volatile oils, and other commonly used dyes of this type wet well the surface of rollers of the invention.

For application in printing, wetting of the surface by various dyes can be varied by a preceding treatment of the surface (total or a part) with agents which modify the surface properties of the swollen polymer. This can be achieved e.g. by short and, if desired, local action of concentrated strong mineral acids, namely sulfuric or phosphoric acid, at suitable temperatures, e.g. around 100°C. Another possibility is a treatment with strong bases, namely with alkaline hydroxides of high concentration, which transform amide and nitrile groups of the surface layer into carboxylate groups. Carboxylic groups may be converted into hydroxamic ones by some of the known chemical reaction, e.g. by transformation into  $\text{—COCl}$  groups with thionyl chloride and subsequent reaction with hydroxylamine. Another possible modification is a transformation of amide groups at the surface into carboxylic groups by means of nitrous acid. As soon as the copolymer contains also carboxylic groups beside the nitrile ones, a further modification can be carried out even e.g. with univalent copper or silver ions. Carboxylic groups can be further employed for a relatively stable ionic crosslinking with chromium(III), aluminium(III) or ferric cations. Amide groups alone may be crosslinked by treatment with aldehydes in an acid medium and higher aldehydes increases the affinity to fatty dyes due to their longer alkyl group. All chemical modifications can be generally used which increase or decrease hydrophilicity of the surface. These modifications can be carried out either at the whole surface, or only that part of the surface is modified, which has to, or must not, accept the dye and the dye is then only applied uniformly on the printing roller.

For the original copolymer solutions, generally known solvents for polyacrylonitrile, e.g. concentrated nitric acid, dimethylformamide, dimethylsulfoxide, or cyclic ethylene carbonate, are suitable when mixed with water, or acetone. Also concentrated aqueous solutions of salts from Hoffmeister series may be used, as e.g. zinc chloride, sodium or calcium thiocyanate, or lithium bromide, either alone or in mixtures with other water-soluble salts which solutions do not dissolve acrylonitrile copolymers but which, up to a certain concentration do not precipitate solution of the copolymer in the aforesaid aqueous salt solutions (e.g.  $\text{ZnCl}_2$ ).

Some copolymers, e.g. copolymers of acrylonitrile with acrylic or methacrylic acid transformed into corresponding salts by

neutralization are soluble also in water and a diluted mineral acid has to be used as the coagulant which contains advantageously a suitable crosslinking or curing agent, e.g. chromium(III), aluminium(III), a ferric salt a suitable aldehyde, or a diisocyanate.

The invention is further illustrated in the following non-limiting Examples.

#### Example 1

Into a 40°C solution of 30 wt. parts of acrylonitrile in 320 parts of water freed from oxygen, 5 wt. parts of methacrylic acid and a redox type polymerization catalyst, consisting of equal amounts (i.e. 2 parts) of 5% aqueous solution of potassium pyrosulfite and ammonium peroxodisulfate, respectively, are added together with 0.5 part of 0.1% solution of copper sulfate. The polymerization is carried out under an inert atmosphere with stirring. Every 2 hours, methacrylic acid is added in four portions by 4 parts, always with 0.25 part of the above mentioned copper sulfate solution. The last portion of methacrylic acid is added with 1 part from both mentioned solutions of pyrosulfite and peroxodisulfate. The resulting heterogeneous mixture contains a part of the copolymer as a coagulate and the remainder as a dispersion and solution. To the cooled mixture, 8 wt. parts of sodium hydroxide pellets is gradually added with cooling and stirring of the solution. The viscous solution of copolymer sodium salt obtained after complete dissolution of NaOH was applied in a thin layer on a metal frame of a gilding roller, which was previously covered with a layer of polyester knitted fabric or linen fixed to the frame by means of a waterfast glue, such as epoxide adhesive.

The roller is slowly revolved and the copolymer solution is applied before its top by means of a common doctor blade adjusted by a micrometer screw to form a thin uniform layer. The roller dips by its lower half into a 5% aqueous solution of potassium aluminium sulfate, which is acidified by 0.5% of sulfuric acid which constitutes the coagulant. The excess is wiped from the exposed part of the roller by a porous rubber roller. Above this roller, another porous cylinder revolves which is sprinkled with water and the roller is blown by warm air before a further copolymer layer is applied. Revolving and layer application continue the elastic swollen layer of required thickness is achieved. At the end of application, the doctor blade is tightened for one complete revolution. The roller is then stopped, removed and washed in water. Then it is placed into a swelling agent consisting of a mixture of 35 volume parts of dimethylsulfoxide, 60 parts of diethylene glycol and 5 parts of distilled water for several days. After use, the roller is placed into this swelling

agent mixture again. If the relative humidity of air does not drop permanently below 55%, the roller surface retains its properties during all the operation period. The same swelling agent mixture is used also for washing the roller which is kept therein when out of operation.

#### Example 2

Using the same equipment as in Example 1, a copolymer solution was applied, which was prepared by the partial hydrolysis of polyacrylonitrile in the following way: Acrylonitrile (150 wt. parts) and 1 part of urea are dissolved in 845 parts of nitric acid of density 1.400 and free of nonbound nitrogen oxides. Ammonium peroxosulfate is then added as 4 parts of 5% aqueous solution and the mixture is thoroughly stirred under an inert atmosphere. Then it is allowed to stand at 20°C for 200 hr without access of oxygen and actinic light. The obtained viscous solution of a acrylonitrile/acrylamide copolymer is applied onto a roller frame made of polypropylene and textile laminate, water being used as the coagulant. Further processing is analogous to Example 1, except the roller is finally placed in swelling agent consisting of a mixture of 60 volume parts of diacetone, 35 parts of dimethylsulfoxide and 5 parts of water.

#### Example 3

The procedure according to Example 2 is repeated with the distinction that the mixture is allowed to stand for 240 hours instead of 200 hours and that a 5% aqueous solution of aluminium nitrate  $Al(NO_3)_3 \cdot 9H_2O$  is used as the coagulation bath, which has been acidified with sulfuric acid until the disappearance of turbidity. The roller is then washed with clear water to remove the acid reaction and stored in swelling agent consisting of a mixture of 30 parts of dimethylsulfoxide, 60 parts of glycerol and 10 parts of water for several days. The same mixture is used for storage after use of the roller. The crosslinking with aluminium limits the swelling and enhances the strength of the layer. It is stable at pH 2 to 7 but is broken at higher pH.

#### Example 4

The solution of partially hydrolyzed polyacrylonitrile in nitric acid, obtained according to Example 2 is extruded through an opening of 1.4 mm in diameter into an excess of tap water as coagulant. The coagulated copolymer in a form of a thick monofilament is washed in water, immersed into 1% aqueous solution of sodium bicarbonate for 1 hour, and again thoroughly washed in distilled water. Excess water was allowed to drop off the swollen copolymer which was then dissolved to a 10–12% solution in di-

methylformamide. The dissolution is assisted by heating to 60–75°C and stirring and takes usually several hours. The resulting viscous solution is applied in a thin layer onto a slowly revolving roller, as described in Example 1. The coagulant is here a mixture of dimethyl-formamide, water and ethylene glycol in ratio 5:2:3. The constant composition of the bath is kept by gradual addition of ethylene glycol, while other components are supplied by the coagulating polymer solution. The roller is stored in the bath of the same composition if out of operation which bath also constitutes the swelling agent.

#### Example 5

Acrylonitrile (10 wt.%) and the same amount of acrylic acid (freed from a polymerization inhibitor) are dissolved in pure benzene, 0.1% of dibenzoyl peroxide is added and the mixture is heated to 70°C for several hours under a reflux condenser and a moderate stream of nitrogen, which is led above the solution surface. A grainy precipitate of the copolymer is several times washed with benzene and dried; the drying is completed in a vacuum oven. The copolymer (one part) is mixed with eight parts of water and solid sodium hydroxide is gradually added under stirring and cooling in the total amount required for complete dissolution which, however, does not exceed the amount corresponding to 0.9 equivalents of acrylic acid used. Water with 1 wt. % of concentrated hydrochloric acid and 1% of 37% formaldehyde serves as the coagulant. After the copolymer application has been completed, the roller is placed without previous washing into a sealed large vessel made from stainless steel, polyethylene or polypropylene, where the temperature 80°C is kept for 4 hours. The roller is then cooled, thoroughly washed with water and without drying stored for several days in a mixture of 20 parts of cyclic ethylene carbonate, 15 parts of dimethylsulfoxide, 10 parts of water and 55 parts of triethylene glycol as swelling agent. It is stored in the same mixture if it is out of operation.

#### Example 6

Polyacrylonitrile prepared by the known precipitation polymerization of acrylonitrile in water by means of a redox initiator is filtered, washed, dried, ground and rapidly dispersed in 70% nitric acid –42°C cold together with 1% of urea. The dispersion containing 10 wt.% of the polymer is allowed to warm slowly to the ambient temperature under continuous stirring, to form a viscous solution which is then slowly heated to 45°C and maintained for 6 hours at this temperature whereupon partial hydrolysis occurs to form an acrylonitrile/acrylamide copolymer.

The solution is then shortly degased, applied layer to layer onto the roller and coagulated with water as in Example 2. Further processing is similar as in Example 1.

#### Example 7

A solvent is prepared by mixing 3 wt. parts of 70% aqueous solution of zinc chloride with 1 wt. part of concentrated aqueous solution of calcium chloride. Acrylonitrile (9 wt.%), 1 wt.% of methacrylamide and 5% of solid sodium ethylenesulfonate, prepared by a rapid vacuum evaporation of its 20% aqueous solution, are dissolved in the above mixture. Then, 0.2% of urea is added and the solution is acidified to pH 2.5 by a small amount of hydrochloric acid. After the gas evolution ceased, the solution is degased in vacuo at the ambient temperature and cast in a thin layer onto a printing roller which dips into a coagulation bath formed by 0.5% solution of sodium bicarbonate. After the application is finished, the roller is washed in 0.2% hydrochloric acid, then in a fresh solution of bicarbonate of the same concentration and finally thoroughly in water. It is stored in some of the mixtures described in preceding Examples to keep the copolymer swollen and prevent its drying in air.

#### Example 8

Freshly distilled anhydrous acrylonitrile (160 g) was dissolved in 840 g of 71% nitric acid. Then, 1.3 g of urea dissolved in 2 ml of distilled water, 3 ml of 5% aqueous ammonium peroxodisulfate and 0.5 g of scorbic acid in concentrated aqueous solution were stirred into this solution. The solution was thoroughly homogenized under exclusion of the oxygen access and allowed to stand in an one liter pipette for 24 hours in darkness, without stirring, at the external temperature 20°C. The pipette was then placed in a box thermostated to 8°C for 16 days whereupon partial hydrolysis occurred to form on acrylonitrile/acrylamide copolymer. The highly viscous solution was applied to a cylindrical roller by the procedure described in Example 1. The roller was thoroughly washed first with tap water, then with a dilute solution of sodium bicarbonate and with distilled water. Then it was placed for 48 hours into a mixture consisting of 70% of glycerol and 30% of water and finally for 24 hours into pure glycerol. The highly elastic and strong polymer is storable without limitation in this form. The roller is suitable for printing and application of gilding or platinating solution in ethereal oils on glass or ceramic articles.

#### Example 9

The procedure according to Example 8 was repeated with the distinction that the solu-

tion in pipette was thermostated to 20°C for 8 days and that the heavily swollen gel obtained after application to the roller and washing was placed into a 5% aqueous solution of chromium(III) sulfate at 20°C for 8 hours. The swelling degree dropped considerably to the value corresponding approximately to the gel according to Example 8. The roller with the light green gel layer was thoroughly washed with water, placed for 48 hours into a mixture consisting of 65% of ethylene glycol and 35% of water, then for 24 hours into a mixture of 85% of ethylene glycol and 15% of water, and finally into pure ethylene glycol. The roller had similar properties and found similar application as the roller according to Example 8.

In all given examples, acrylonitrile may be substituted with methacrylonitrile in part, preferably up to 10 wt.%. Another monomers which can be added either singly or in combinations approximately up to 50 wt.% of used acrylonitrile, are acrylamide, methacrylamide, N-alkylacrylamides and N-alkylmethacrylamides, glycol monoacrylates and glycol mono-methacrylates, ethoxyethyl acrylate and methacrylate, sodium ethylenesulfonate, etc. Most advantageous are such copolymers which contain at least 30 mole % (preferably at least 50 mole %) of the acrylonitrile component, irrespective of their preparation by copolymerization, partial hydrolysis, or combination of both these processes. The gels obtained by the partial hydrolysis of polyacrylonitrile in a homogeneous acid medium, e.g. in concentrated nitric acid, are superior to others by their remarkable strength and resistance to a mechanical damage.

#### WHAT WE CLAIM IS:—

1. A roller comprising a cylindrical core formed of material which does not swell in water, and an outer cylindrical packet made from a water insoluble elastic gel comprising a copolymer of acrylonitrile and at least one further monomer selected from simple or substituted acrylamide and methacrylamide, acrylic and methacrylic acid, ethylenesulfonic acid or salts of the aforesaid acids, and a swelling agent which contains at least one compound coloured from water, alkylene glycols and polyalkylene glycols, where alkylene is ethylene, propylene or butylene, their methoxy and ethoxy derivatives, glycerol and its acetyl derivatives, phenols, aromatic alcohols, hydroaromatic alcohols, aliphatic alcohols  $C_1-C_{14}$  and esters of the aforesaid alcohols and ethers, fatty acids and their salts and esters.

2. A roller as claimed in claim 1 wherein the cylindrical core is formed of metal, plastics material, hard rubber or ceramic material.

3. A roller as claimed in claim 1 or 2

wherein the swelling agent contains a minor amount of dimethyl formamide, dimethyl sulphoxide or cyclic ethylene carbonate.

4. A method of manufacturing the roller according to claim 1, wherein a layer of the copolymer in a solvent is applied onto the cylindrical core and the copolymer is coagulated in a bath which contains a coagulant comprising at least one compound selected from water, lower aliphatic alcohols  $C_1-C_4$ , acetone, dioxane, benzylalcohol, alkylene glycols  $C_2-C_4$  and polyalkylene glycols, alkylene glycol methoxy and ethoxy derivatives, glycerol and its acetyl derivatives, wherein the copolymer solvent or the coagulant constitutes said swelling agent, or the roller is subsequently treated with said swelling agent.

5. A method as claimed in claim 4, wherein the copolymer solution is applied layer by layer and each layer is applied after the preceding layer has been coagulated and the excess coagulation liquid has been removed.

6. A method as claimed in claim 5, wherein the core is rotated about its axis which is horizontally orientated, the copolymer solution is applied to the rotating roller at one region and the layer formed is brought into contact with the coagulating liquid at another region.

7. A method as claimed in claim 5

wherein the copolymer is cross-linked by action of an agent selected from trivalent chromium, trivalent aluminium, trivalent iron, univalent copper, univalent silver, aldehydes and polyisocyanates.

8. A method as claimed in claim 7, wherein the agents act only at certain parts of the roller surface.

9. A method as claimed in claim 4, wherein after coagulation, the roller surface is treated with an agent selected from mineral acids, aqueous solutions of alkaline hydroxides, nitrous acid, and thionyl chloride with subsequent treatment with hydroxylamine.

10. A method as claimed in claim 9, wherein the agents act only at certain parts of the roller surface.

11. A roller as claimed in claim 1, substantially as hereinbefore described with reference to any one of the accompanying examples.

12. A method as claimed in claim 4, substantially as hereinbefore described.

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